NUKLEONIKA 2013;58(1):113–116

ORIGINAL PAPER

Phase constitution of an $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy investigated by Mössbauer spectroscopy

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Abstract. In the present work the phase constitution and magnetic ordering of the magnetocaloric $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy in the as-cast state and after annealing at 1323 K for 1 h (in case of ribbons) and 49 days (in case of bulk) were studied. For bulk and ribbon samples in as-cast state three crystalline phases were identified: dominant ferromagnetic α-Fe, minor ferromagnetic La(Fe,Co)Si and traces of paramagnetic $La(Fe,Si)_{13}$ phase. Appropriate heat treatment resulted in the evolution of phase constitution of the alloy, where two crystalline phases were developed: the dominant paramagnetic $La(Fe,Si)_{13}$ phase and a minor fraction of the ferromagnetic α-Fe for both bulk and ribbon samples.

Key words: magnetocaloric materials • Mössbauer spectroscopy

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Received: 11 June 2012
Accepted: 14 September 2012

Introduction

Research on new magnetic materials, revealing a large magnetic entropy change $|\Delta S_M|$, and the Curie point T_C around room temperature, was intensified since the discovery of a giant magnetocaloric effect (GMCE) in $Gd_5Si_2Ge_2$ alloy [9]. Here, under the change of external magnetic field $\mu\Delta H = 5$ T, $|\Delta S_M|$ reaches 18.5 J/(kg·K) at around T_C of ~276 K [9]. Over the last decade the research was focused on $La(Fe,Si)_{13}$ alloys. Due to the high iron content (~80 at.%), these materials are relatively cheap and reveal good magnetocaloric properties at room temperature. Depending on the composition and heat treatment, these alloys can form two different structures: tetragonal or cubic. The high magnetocaloric effect was revealed for crystalline cubic $NaZn_{13}$-type phase (space group *Fm*3*c*) [7, 8]. Furthermore, appropriate admixture results both in the change of Curie temperature T_C and magnitude of the magnetocaloric effect [4, 5, 10]. Magnetic entropy change $|\Delta S_M|$ reaching up to 31 J/(kg·K) is not only the effect of transition from ferro- to paramagnetic state, but also the first order phase transition around T_C. High temperature annealing of these alloys results in evolution from dendritic in the as-cast state to the fully homogenized microstructure [1]. Furthermore, processing route can impact the annealing time needed for obtaining appropriate phase constitution and magnetocaloric effect [2]. Our earlier studies have also shown that admixtures of Al or Ga can affect the Curie point [3]. The aim of the present work was to investigate the phase constitution

and magnetic ordering in bulk and ribbon samples of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy.

Sample preparation and experimental techniques

The ingot sample was obtained by arc-melting of high purity elements under inert gas atmosphere (Ar). Master alloy was prepared for stoichiometric composition corresponding to formation of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ phase. From part of the ingot, the ribbon samples were prepared by melt-spinning technique under the Ar atmosphere with a copper wheel speed of ~35 m/s. Bulk and ribbon specimens were sealed-off in quartz tubes under low pressure of the Ar and subsequently annealed at 1323 K for 1 h (in the case of ribbons) and 49 days (for bulk samples). X-ray diffraction was carried out using a Bruker D8 Advance diffractometer (with CuKα radiation) equipped with a LinxEye semiconductor detector. Theoretical diffraction patterns were simulated and fitted to experimental data with PowderCell 2.4 [6] software. Mössbauer spectra were measured using a Polon Mössbauer spectrometer with a ^{57}Co:Rh source in transimission geometry and subsequently analysed using WinNormos for Igor software. The samples were subjected to the mechanical polishing and etching for 3 s in a 0.5% Nital solution in order to reveal microstructure using a metallografic microscope NEOPHOT-32.

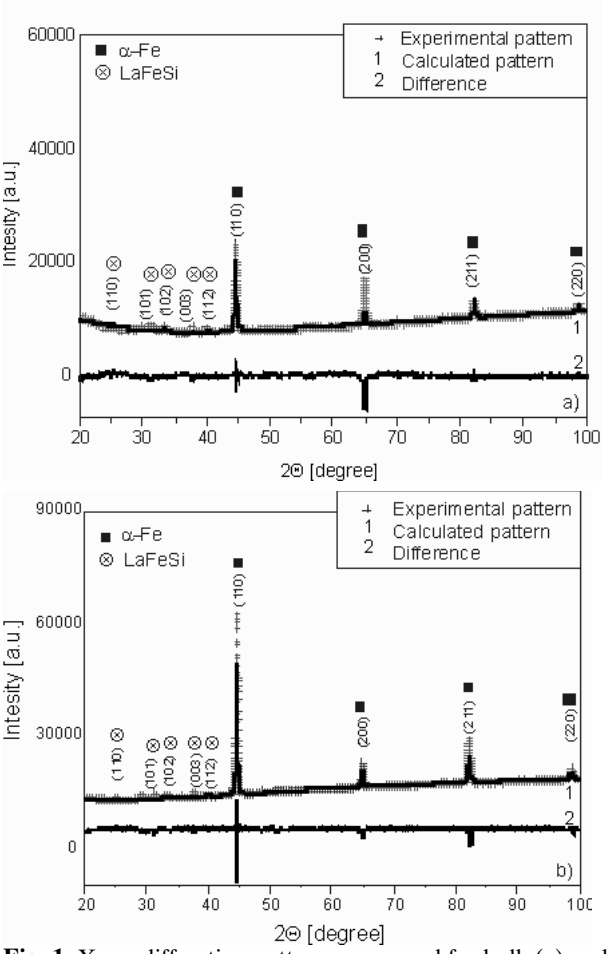

Fig. 1. X-ray diffraction patterns measured for bulk (a) and ribbon samples (b) of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy in as-cast state.

Results and discussion

The X-ray diffraction scans measured for bulk and ribbon samples of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy in as-cast state together with the calculated theoretical diffractions, are shown in Fig. 1.

The analysis carried out for both as-cast samples shows that the main crystalline phase formed during solidification from melt is the α-Fe, that coexists with the tetragonal LaFeSi phase of the space group *P*4/*nmm*. Calculated contributions show that 92% and 93% of the volume, respectively, for bulk and ribbon samples is attributed to the α-Fe phase. The rest of material is composed of the LaFeSi phase. Corresponding cell parameters calculated for constituent phases show similar values for both bulk and ribbon samples. For α-Fe phase the lattice constant $a = 2.86$ Å in both cases, while for the LaFeSi phase – $a = 4.07$ Å and $c = 7.15$ Å for bulk samples and $a = 4.09$ Å and $c = 7.20$ Å for the ribbon. Such small discrepancies may by due to the different conditions of the sample preparation.

The X-ray diffraction patterns measured for the annealed samples, are shown in Fig. 2. It was revealed that the heat treatment resulted in a significant change of the phase constitution. As an effect of annealing, the cubic $NaZn_{13}$-type phase of the space group *Fm*3*c* was formed. It was shown that ~97 vol.% of the $NaZn_{13}$-type phase is formed for bulk sample, while for ribbons the formation of this phase decreases to 63 vol.%.

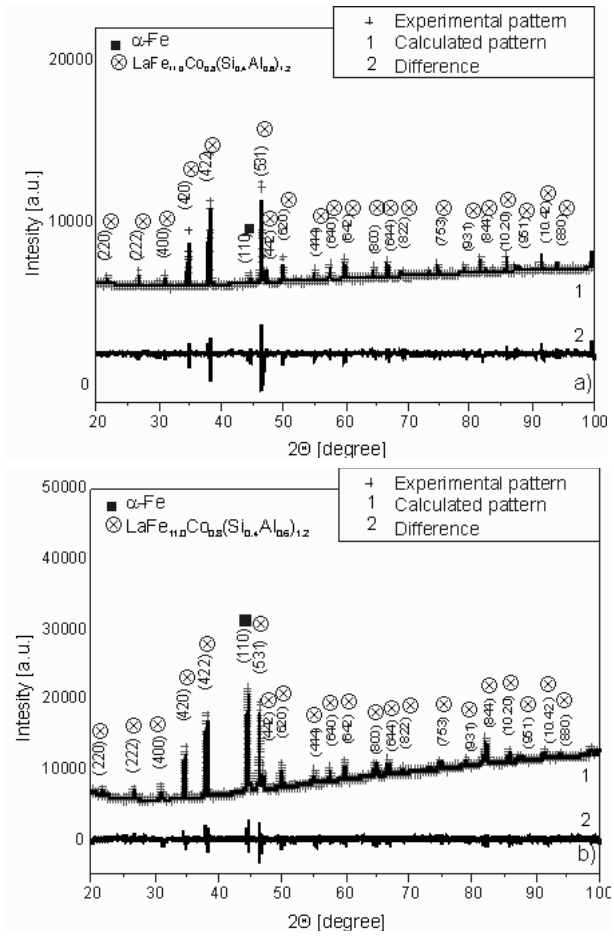

Fig. 2. X-ray diffraction patterns of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy subjected to annealing at 1323 K for 49 days for bulk sample (a) and 1 h for ribbon (b).

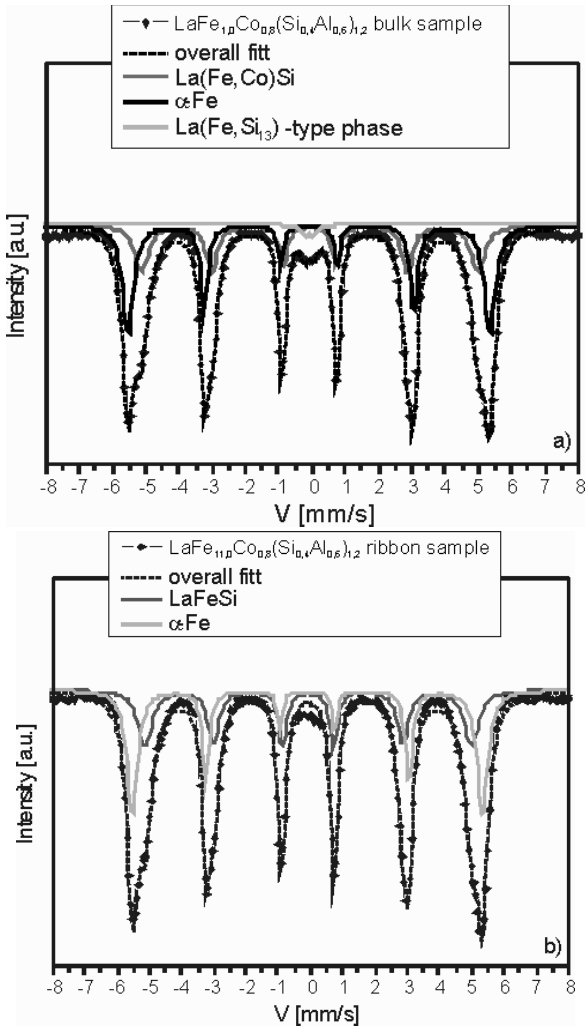

Fig. 3. Mössbauer spectra measured for the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy in as-cast state in a form of bulk (a) and ribbon (b) samples.

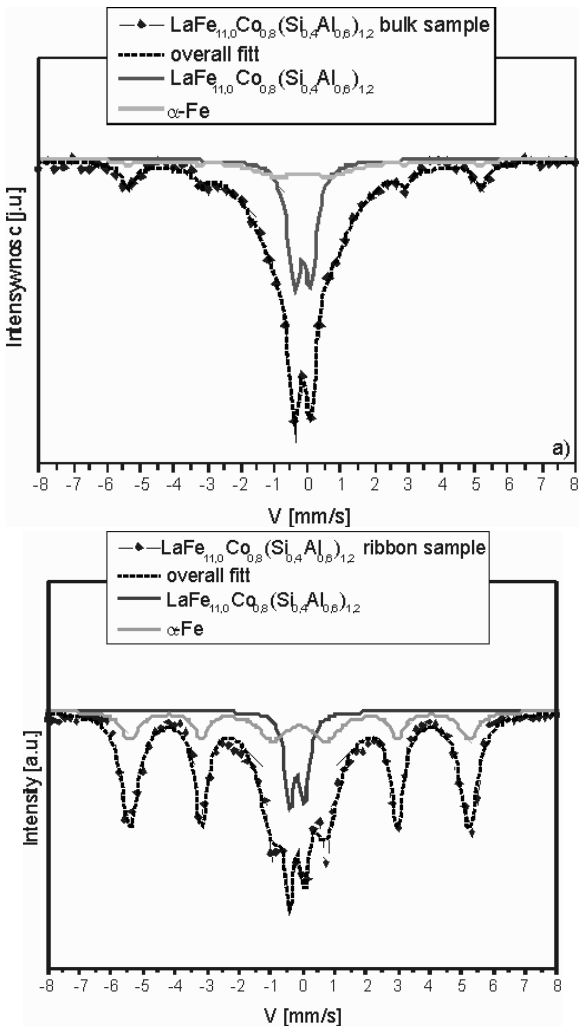

Fig. 4. Mössbauer spectra measured for the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy bulk sample annealed at 1323 K for 49 days (a) and ribbon annealed for 1 h (b).

In both cases the rest of the volume is occupied by α-Fe phase. The calculated lattice constant a for the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ phase of $NaZn_{13}$-type reaches 11.55 Å for bulk and 11.56 Å for ribbon, respectively, while lattice constant determined for α-Fe was equal to 2.86 Å in both samples.

In Figure 3 the Mössbauer spectra measured of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy in as-cast state for bulk and ribbon samples are presented. Analysis of Mössbauer spectrum for the bulk sample has shown the presence of two ferromagnetic phases: α-Fe and LaFeSi in the alloy constitution. Furthermore, a doublet which was attribute to paramagnetic phase was revealed. This can be related to the presence of nuclei of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ phase. The volume fractions of constituent phases are 51 vol.% for α-Fe, 46 vol.% for LaFeSi and 3 vol.% for $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ phase.

The Mössbauer spectra for ribbon annealed for 1 h and bulk sample annealed for 49 days are shown in Fig. 4.

The analysis has shown the coexistence of dominant paramagnetic $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ and remanent ferromagnetic α-Fe phases. It was shown that for the long-time annealed bulk sample about 85% of the volume is occupied by the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ phase. Much smaller fraction (66 vol.%) was formed during short-time annealing of ribbon.

Microstructure of the as-cast $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ bulk and ribbon samples are shown in Fig. 5. Both samples revealed dendritic microstructure, where dendrites were formed by α-Fe phase, while other alloy components were expelled into the dendrite arm spacing. For ribbon sample the dendrite arms have smaller widths than that for bulk sample. Such a change of microstructure is caused by different cooling rates during solidification of bulk samples and ribbons.

The microstructures of bulk and ribbon samples of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy subjected to annealing at 1323 K were shown in Fig. 6. Heat treatment carried out for both specimens caused homogenization of their microstructure.

Conclusions

The X-ray diffraction for the as-cast $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy show crystallization of cubic α-Fe and tetragonal LaFeSi phases. For bulk specimens, Mössbauer spectra analysis revealed that except α-Fe and LaFeSi a small amount of paramagnetic $NaZn_{13}$-type phase is also present. Annealing of the

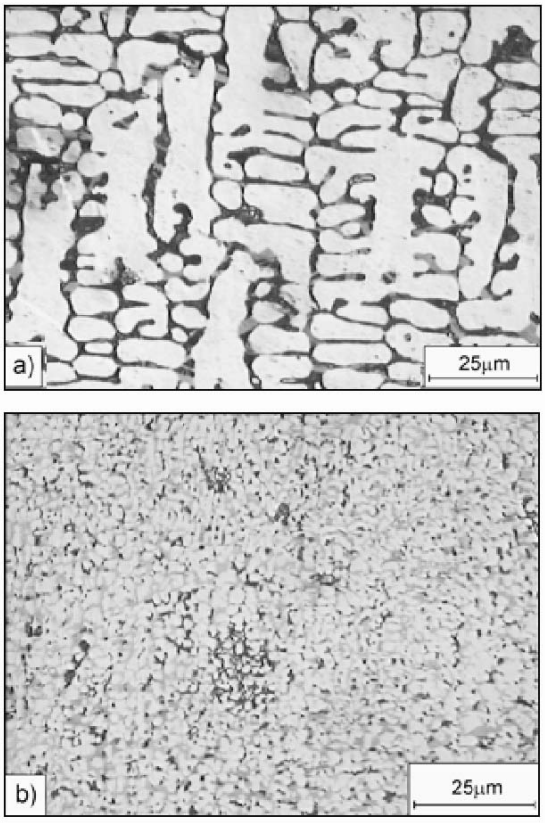

Fig. 5. Microstructure of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ alloy in as-cast state for bulk (a) and ribbon (b) samples.

samples resulted in a change of the phase constitution and formation of paramagnetic $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ phase coexisting with small quantity of the ferromagnetic α-Fe. Application of melt-spinning technique allowed crumbling of microstructure, thus causing acceleration of formation of the $NaZn_{13}$-type phase. However, the major drawback is a smaller contribution of this phase in alloy constitution.

Acknowledgment. Work supported by the research project N N507 233040 financed by the Polish National Science Centre in years 2011–2014.

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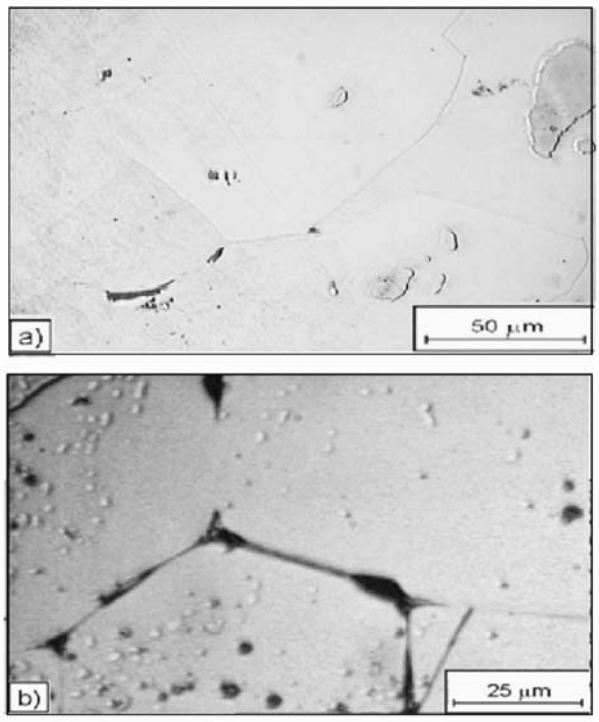

Fig. 6. Microstructure of the $LaFe_{11.0}Co_{0.8}(Si_{0.4}Al_{0.6})_{1.2}$ subjected to annealing at 1323 K for bulk sample for 49 days (a) and ribbon sample for 1 h (b).

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